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# Rice Husk for Photocatalytic Composite Material Fabrication

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Additional information is available at the end of the chapter

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## Abstract

As a semiconductor, zinc oxide (ZnO) has better UV absorbing properties compared to other semiconductor materials, and therefore, it has better dye degrading abilities. However, ZnO tends to agglomerate, which lead to poor degradation compared to the other semiconductors. In this study, to overcome the agglomeration of ZnO, silica (SiO<sub>2</sub>) was combined with ZnO. The composite was tested for its photocatalytic activity. The ZnO/SiO<sub>2</sub> photocatalyst was fabricated on a glass plate. In order to investigate the addition of SiO<sub>2</sub> on ZnO, X-ray diffraction (XRD) and scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDS) was used. The result of the XRD analysis demonstrates similar peak results with ZnO XRD data from ICSD 157132 with a hexagonal structure. The results indicate that the ZnO structure did not change after the addition of SiO<sub>2</sub>, while SEM-EDS results showed that SiO<sub>2</sub> was supported on ZnO with 8% composition. The optimal composition was found to be ZnO/SiO<sub>2</sub> 95/5, as indicated by high degradation activity, which can degrade up to 89% methylene blue.

**Keywords:** rice husk, silica, photocatalysis, ZnO, methylene blue

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## 1. Introduction

The textile industry is developing at a rapid pace, and this has a positive impact on garments development. However, it also increases the negative impact through their industrial waste, especially textile dye. One of the means to degrade dye is by the use of a semiconductor material that has photocatalytic activity [1]. Utilization of semiconductors in photocatalysis is an interesting topic, attributable to its ability to degrade compounds with ultraviolet light facilitation [2].

TiO<sub>2</sub> is usually used as a photocatalyst because it is stable compared to the other photocatalytic agents. However, TiO<sub>2</sub> absorbs less UV light compared to ZnO. Therefore, ZnO can degrade more dye. However, in reality, ZnO degrades less dye compared to TiO<sub>2</sub>, since ZnO tends to agglomerate [3]. To overcome this problem, SiO<sub>2</sub> can be added to ZnO. Pure ZnO degrades 40% dye in 60 minutes. However, when SiO<sub>2</sub> was added, the degradation increased and showed better results compared to pure ZnO. The addition of SiO<sub>2</sub> to ZnO achieved optimum photocatalytic activity at ZnO/SiO<sub>2</sub> 90/10 weight ratio with 99% dye degradation efficiency [4].

Rice husk is composed of about 20% paddy grain [5]. It is composed of mainly cellulose (~32%), silica (~22%) and lignin (~16%) [6]. After milling, rice husk becomes a major waste product, and is not utilized optimally. In 2015, Indonesia produced 75 million tonnes of rice (Central Agency on Statistics, bps.go.id), and therefore, rice husk becomes abundant and a cheap source for silica.

The efficiency of degradation and decolourization is affected by the stability of ZnO layer and ZnO layer morphology. An experiment was conducted by fabricating ZnO/SiO<sub>2</sub> composite with 95/5, 90/10, and 85/15 weight ratio. The results indicated good results when the composite was used to degrade methylene blue with synthetic SiO<sub>2</sub> made from rice husk as the supporting material. Therefore, the present study aims to fabricate ZnO/SiO<sub>2</sub> with less agglomeration [4].

## 2. Experimental section

### 2.1. Isolation of SiO<sub>2</sub>

Rice husk was carbonated at 400°C for 6 hours, followed by increasing the heat to 700°C in an argon atmosphere for 4 hours. The carbon was then ground and seized using a 100 mesh sieve. The carbon was suspended in with a mole ratio 1/3/150 = silica:potassium carbonate: water and refluxed for 150 minutes. The mixture was filtered and the filtrate was allowed to cool. The SiO<sub>2</sub> was precipitated and collected after filtering the solution.

### 2.2. Fabrication of ZnO/SiO<sub>2</sub> nanocomposite

Three weight ratio of ZnO/SiO<sub>2</sub>, namely, 100/0, 95/5, 90/10 and 85/15, were prepared to give 3 g of total mass. The solid mixture was then suspended in 100 mL of distilled water. The suspension was stirred using a magnetic stirrer (500 rpm) for 2 hours, followed by sonication for 90 minutes (Elma ultrasonic LC 30H). The ZnO/SiO<sub>2</sub> suspension was dropped onto a glass slide (1 × 3 cm) with a pipette until the entire glass surface was covered. The slide was dried at 40°C for 12 hours, followed by calcinations at 450°C for 1 hour. The slide was washed using distilled water, and the layer was characterized using X-ray diffraction (XRD) and scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDS).

### 2.3. Determination of maximum wavelength and standard curve

The absorbance of 1 ppm methylene blue solution was recorded at 500–700 nm in wavelength. The wavelength at which the highest absorbance was detected was used to measure the concentration of methylene blue. The standard curve was made by measuring the absorbance of

methylene blue solutions with concentration values of 0.2, 0.4, 0.6 and 0.8 ppm. The absorbance was plotted against concentration, and used as a standard curve.

## 2.4. Photocatalytic assay

For photocatalytic assay, a glass slide with ZnO/SiO<sub>2</sub> layer was inserted into 50 mL of 1 ppm methylene blue in a test tube. It was followed by irradiation using a mercury lamp for 4 hours. Every 2 hours, 2 mL of sample was collected, and its methylene blue content was determined using a visible spectrophotometer at 660 nm. The assay was performed for all the fabricated slides.

## 3. Results and discussions

### 3.1. ZnO/SiO<sub>2</sub> photocatalyst

The ZnO/SiO<sub>2</sub> photocatalyst was fabricated to give final mass of 3 g with 95/5, 90/10, 85/15 weight ratio, as described in previous studies [4, 7]. The fabrication was conducted in distilled water, while assay was performed in two different solvents, i.e., distilled water and methanol. According to the assay results, both solvents yielded the same ZnO attachment level on the glass slide. Therefore, both water and methanol are effective as solvents, as previously proposed [7]. In order for ZnO and SiO<sub>2</sub> to completely disperse in water, the suspension was stirred with a magnetic stirrer at 500 rpm for 2 hours, as recommended by prior work [4].

Sonication with ~30 kHz for 90 minutes was conducted to homogenize the ZnO/SiO<sub>2</sub> so that no agglomeration occurs. Prior to the coating, the glass slide was cleaned using acetone to remove impurities that can interfere with the attachment of ZnO/SiO<sub>2</sub>. The glass slide that was coated with ZnO/SiO<sub>2</sub> was dried in a 40°C oven for 12 hours to remove excess water so that the ZnO/SiO<sub>2</sub> attaches strongly onto the glass slide (**Figure 1**).

To increase the attachment of ZnO/SiO<sub>2</sub> onto the glass slide, it was heated to 450°C. The surface where ZnO/SiO<sub>2</sub> is attached should be a flat surface, so that when the surface is washed it is easier for the agglomerated ZnO/SiO<sub>2</sub> to be washed [4].

### 3.2. Characterization results

SEM-EDS and XRD was performed to investigate the ZnO coating onto glass slides. Complete analysis was performed for ZnO/SiO<sub>2</sub> 95/5 weight ratio. The result of SEM is illustrated in **Figure 2**. It can be observed on the 500× magnification that the ZnO/SiO<sub>2</sub> layer attached uniformly with low porosity. A porous structure started to appear at 1000× magnification. The particles attachment affects the efficiency of methylene blue degradation, since it determines hydroxyl radical generation by ZnO to degrade the dye.

**Figure 3** shows the ZnO layer without SiO<sub>2</sub> addition. It appears that the particles do not attach uniformly, and have a higher porosity compared to the ZnO/SiO<sub>2</sub> layer, as shown in **Figure 2**. It appears that the addition of SiO<sub>2</sub> to ZnO is significantly effective to facilitate a uniform spread

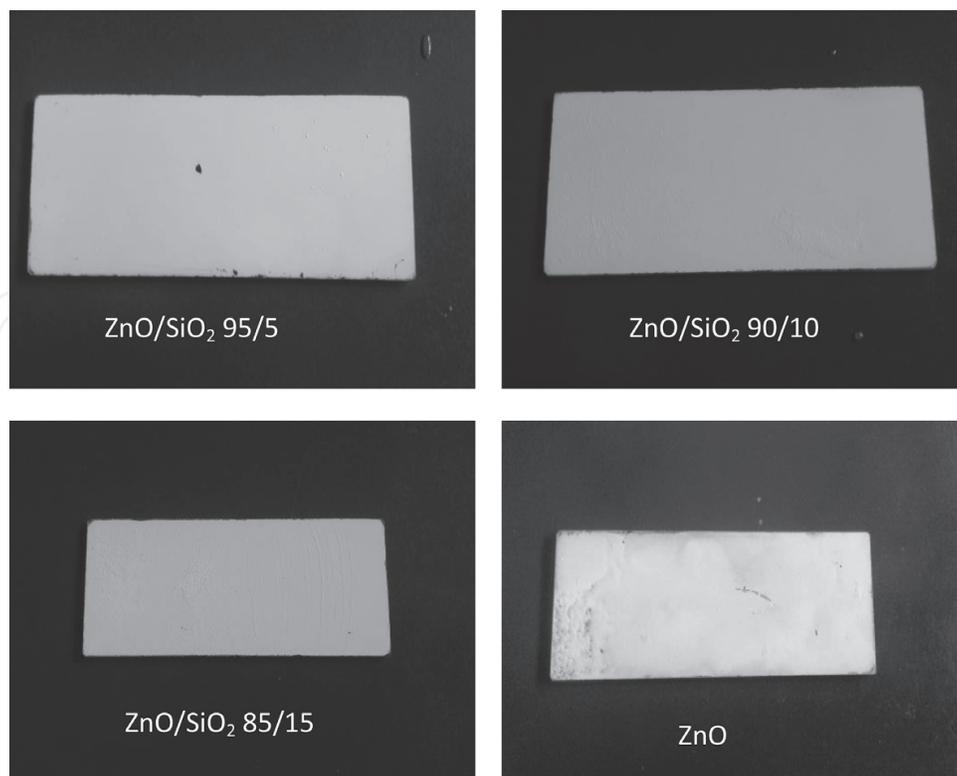


Figure 1. ZnO/SiO<sub>2</sub> and ZnO.

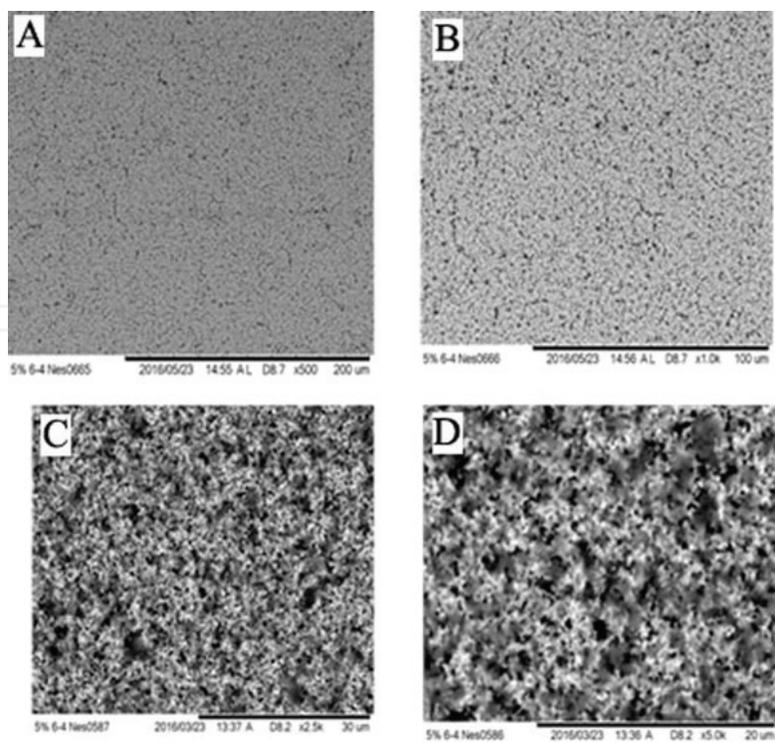
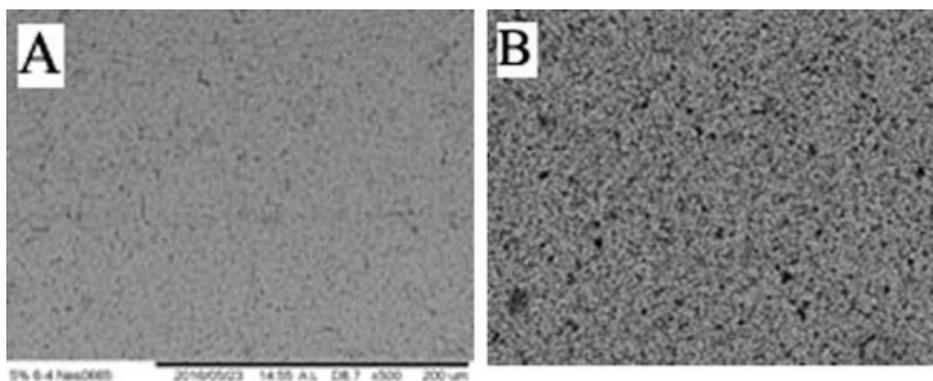


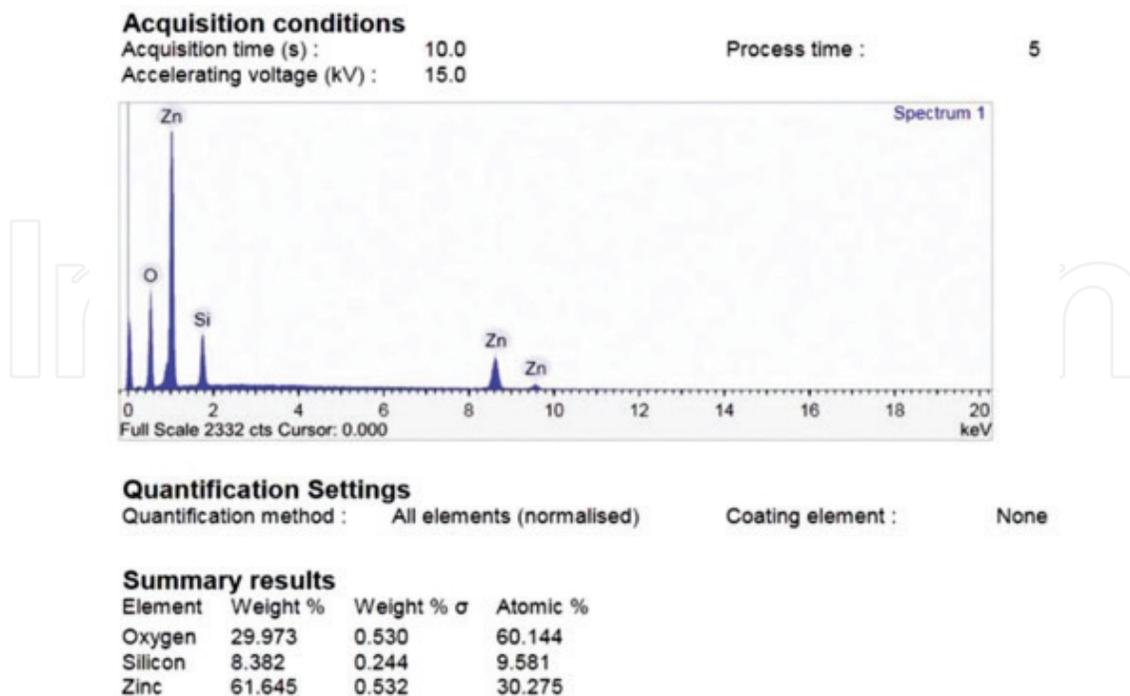
Figure 2. Micrograph of ZnO/SiO<sub>2</sub> at 95/5 weight ratio at (A) 500-, (B) 1000-, (C) 2500-, and (D) 5000-fold magnification.

of ZnO when attached onto the glass slide surface, which can then reduce the porosity of the ZnO/SiO<sub>2</sub> layer. A lower porosity leads to a higher ZnO attached to the glass slide, which acts as a hydroxyl radical generator. Based on the comparison results of ZnO to ZnO/SiO<sub>2</sub> with 95/5 weight ratio, it is clear that the composite can produce more hydroxyl radical, which leads to a more effective dye degradation.

The EDS results are presented in **Figure 4**. EDS is used to investigate the composition of ZnO and SiO<sub>2</sub> in ZnO/SiO<sub>2</sub> mixture. With 95/5 weight ratio, Zn and Si composition was 61.64 and 8.38% weight respectively. However, according to the calculation results, the composition of Zn and Si should be 76.23 and 2.30% weight respectively. A higher Si composition and a lower Zn composition compared to the theoretical value is due to the ZnO being carried



**Figure 3.** Micrograph of (A) ZnO/SiO<sub>2</sub> 95/5 weight ratio and (B) ZnO with 500× magnification.

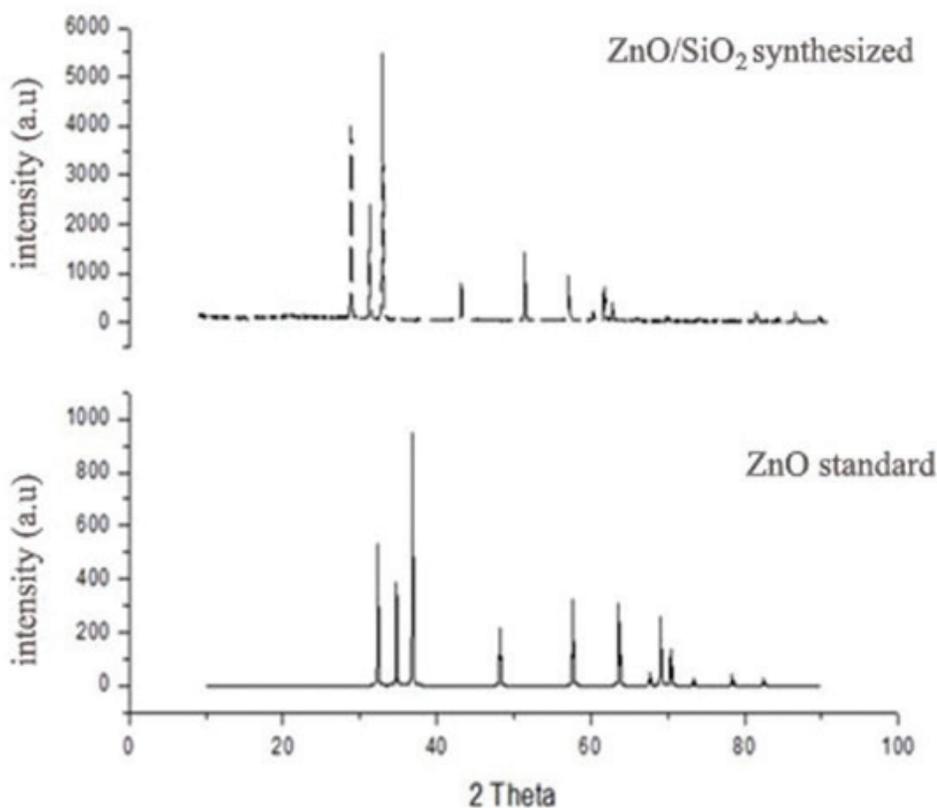


**Figure 4.** EDS results of ZnO/SiO<sub>2</sub> 95/5 weight ratio.

away during the washing process, especially the agglomerated ZnO. The agglomeration may occur when sonication is extensively long. When more ZnO is washed away, a more porous structure occurs on the layer (**Figure 3**). A high porosity on the layer reduces the ability of ZnO to form hydroxyl radical, which then reduces the rate of degradation. From the EDS results (**Figure 3**), it was proven that 8.38% of SiO<sub>2</sub> is supported on the ZnO particles. It was also found that around 1.22% weight was not detected by the EDS method, which indicates the presence of impurities in the layer.

To investigate the effect of SiO<sub>2</sub> on the ZnO structure, XRD was used. The result of XRD is presented in **Figure 5**. It was found that peaks at 32.33°, 34.67° and 36.85° of ZnO/SiO<sub>2</sub> was shifted compared to standard ZnO. This shift occurred as a result of the SiO<sub>2</sub> attachment on ZnO. The intensity of the peaks indicates that there is no difference between peaks of ZnO/SiO<sub>2</sub> compared to standard ZnO (ICSD 157132 standard), which has a hexagonal crystal structure. This result is in agreement with previously published results, which describe that layers of ZnO have a hexagonal structure.

The results indicate that the addition of SiO<sub>2</sub> does not change the ZnO crystal structure. However, the addition of SiO<sub>2</sub> can increase the distribution of ZnO on the glass slide, thus resulting in a more homogen layer, which leads to no agglomeration. The XRD of ZnO/SiO<sub>2</sub> shows that the SiO<sub>2</sub> peak appears with very low intensity at 2θ = 20–25° (**Figure 5**). The low intensity peak appears because the SiO<sub>2</sub> amount in ZnO/SiO<sub>2</sub> was low, i.e. 5%. The peak at 2θ = 23.5° with low intensity belongs to SiO<sub>2</sub> from rice husk with an amorphous property.



**Figure 5.** XRD of ZnO/SiO<sub>2</sub> and ZnO standard (ICSD 157132).

This result confirmed that  $\text{SiO}_2$  used to fabricate  $\text{ZnO}/\text{SiO}_2$  is  $\text{SiO}_2$  from rice husk with an amorphous property (Figure 6).

### 3.3. Maximum wavelength and standard curve of methylene blue

The wavelength at which maximum absorbance of methylene blue was detected is 660 nm. The maximum wavelength has the highest sensitivity, and therefore the measurement of methylene blue concentration was conducted at this wavelength to minimize error rate. The correlation of the standard curve was 0.9909, which shows that the method has good correlation.

### 3.4. Photocatalysis assay

In the photocatalysis assay, samples were collected four times every hour, and the concentration of methylene blue was determined by measuring the absorbance of the samples and converted to a concentration using a standard curve. The percentage of the efficiency of methylene blue degradation was obtained by comparing the concentration of methylene blue before and after radiation. The efficiency of degradation is presented in Figure 7.

As shown in Figure 7, after 1 hour of radiation,  $\text{ZnO}/\text{SiO}_2$  with 95/5 weight ratio was more effective compared to the other samples, as it can degrade up to 52.5% of methylene blue. After 3 hours of irradiation,  $\text{ZnO}/\text{SiO}_2$  with 90/10 weight ratio degrades the dye better compared to the other samples. After 4 hours of irradiation,  $\text{ZnO}/\text{SiO}_2$  photocatalysts with weight ratio of 95/5, 90/10 and 85/15 showed 89.95, 82.57 and 37.40% degradation percentage respectively. The photocatalysts with 95/5 and 90/10 weight ratio is more effective in degrading methylene blue dye compared to 85/15 weight ratio, as indicated by percentage degradation above 80%. When  $\text{SiO}_2$  was used by more than 10%, the ability of the photocatalysts became lower. This is likely caused by  $\text{SiO}_2$  covering  $\text{ZnO}$  that should be act as photocatalysts, which leads to a lower hydroxyl radical formation.  $\text{ZnO}/\text{SiO}_2$  photocatalysts with 85/15 weight ratio

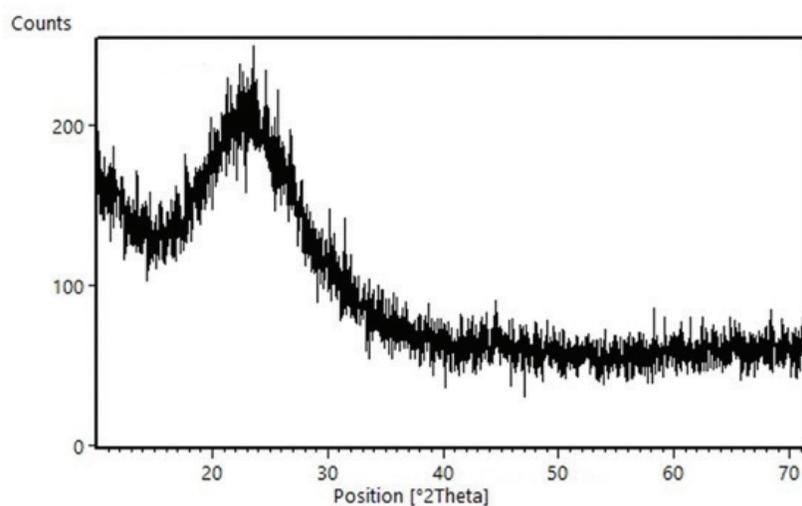


Figure 6. XRD of  $\text{SiO}_2$ .

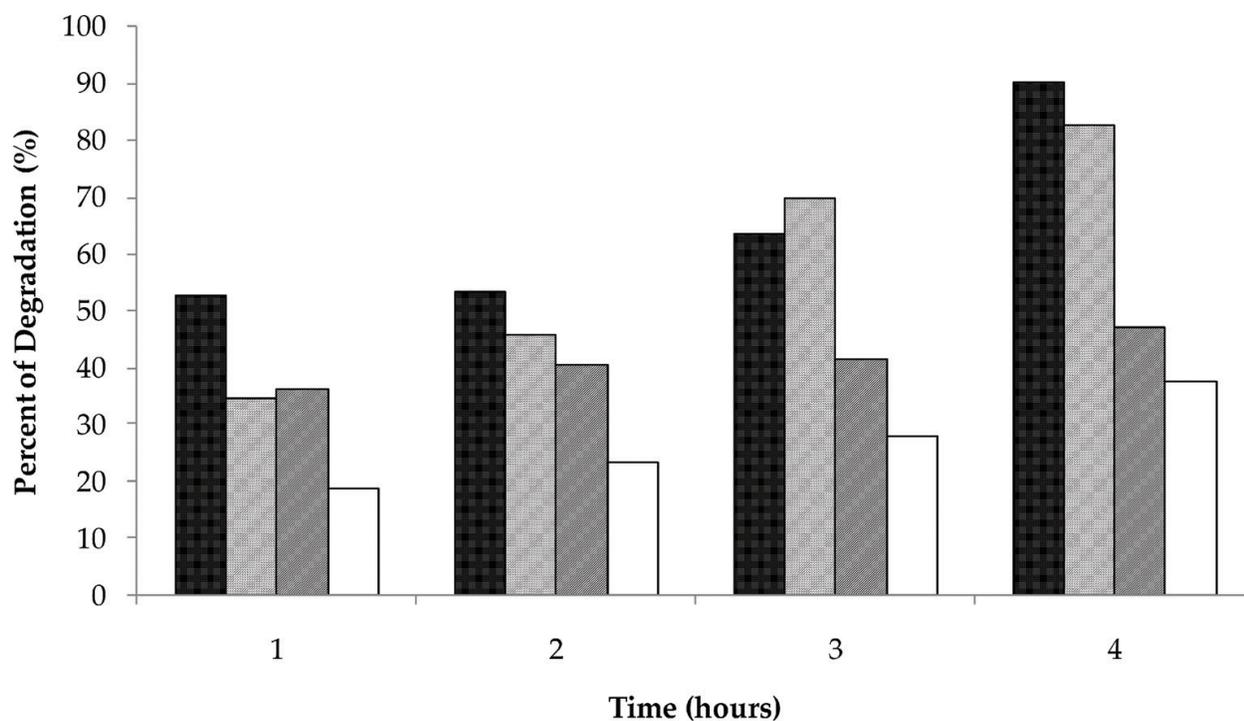


Figure 7. Efficiency of methylene blue degradation using ZnO/SiO<sub>2</sub> photocatalysis with various ZnO/SiO<sub>2</sub> weight ratio. Irradiation time was 4 hours.

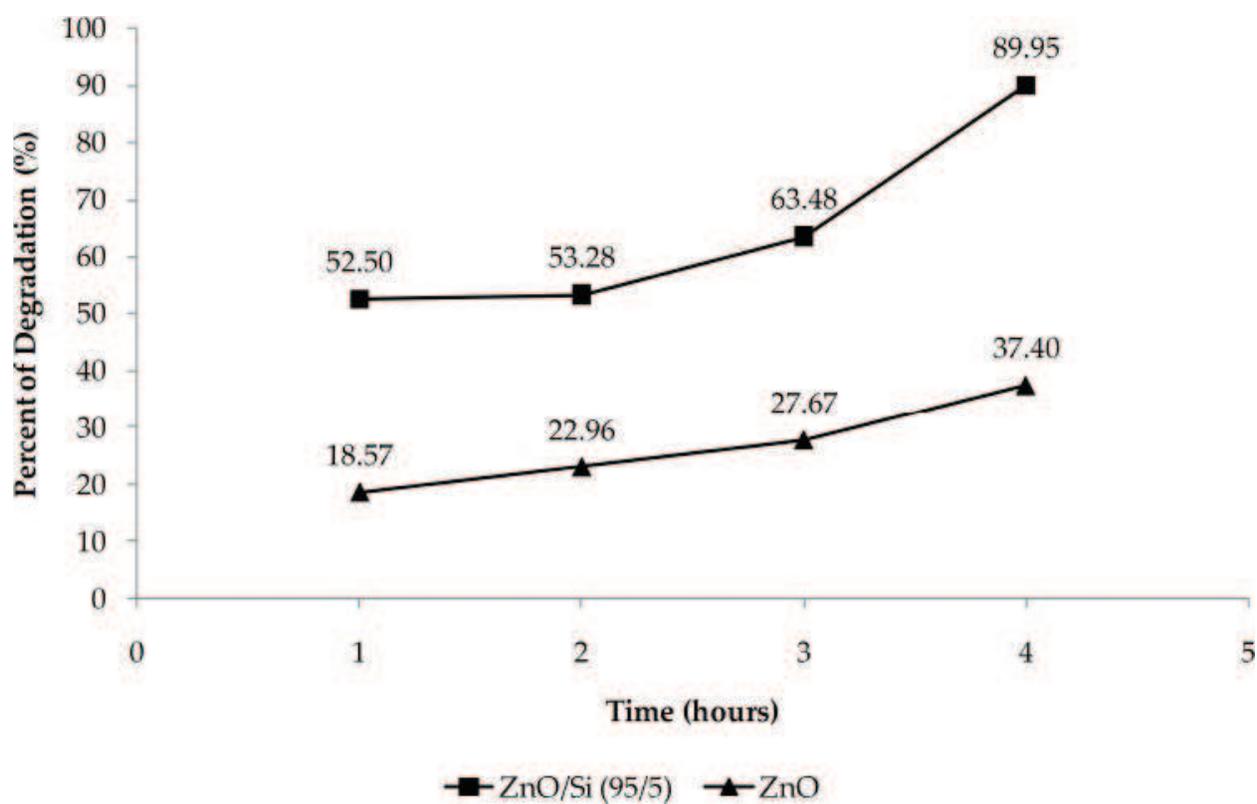


Figure 8. Comparison of methylene blue degradation efficiency using ZnO/SiO<sub>2</sub> compared to ZnO photocatalyst.

less efficient because  $\text{SiO}_2$  is not a semiconductor material, so it cannot produce free electrons and hydroxyl radicals. According to Behnajady et al. [8], less hydroxyl radicals will lead to a lower dye reduction efficiency. **Figure 7** confirms this, where photocatalysts with 95/5 weight ratio showed the highest dye degradation.

**Figure 8** shows the comparison between  $\text{ZnO/SiO}_2$  and  $\text{ZnO}$  photocatalytic activity. It is clear that the addition of  $\text{SiO}_2$  increases the effectiveness of the photocatalyst, as indicated by higher methylene blue degradation of up to 89.95%, while  $\text{ZnO}$  without  $\text{SiO}_2$  can only degrade 37.40%. According to Soltani et al. (2015), this is caused because the  $\text{ZnO}$  attachment without  $\text{SiO}_2$  was not uniform on the glass slide surface that tends to form a porous structure. The addition of  $\text{SiO}_2$  to  $\text{ZnO}$  assisted the attachment to form a uniform layer, and this leads to lower porosity.

## 4. Conclusion

The addition of silica from rice husk to  $\text{ZnO}$  photocatalysts improves the spread of the particles uniformly on the glass slide. The addition of the silica does not alter the crystal structure of the  $\text{ZnO}$ . The optimal composition was found to be  $\text{ZnO/SiO}_2$  95/5, as indicated by a high degradation activity, which can degrade up to 89% methylene blue.

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